

- TITLE:** PROCEDURE TO CONVERT OP-FTIR VOLUME-CONCENTRATION DETERMINATIONS OF ALKANE MIXTURE THAT ORIGINATE FROM PETROLEUM-BASE FUELS TO MASS CONCENTRATIONS.
- SCOPE:** Describes the Optical Remote Sensing (ORS) analytical method for determining the mean molecular mass of alkane mixtures that are emitted from petroleum-based fuels.
- PURPOSE:** Quantitative measurements by OP-FTIR of vapors and gases are determined as volume path-integrated concentrations (VPICs). The use of VRPM for the purpose of determination of emission fluxes and/or emission rates required the conversion of the VPIC to mass path-integrated concentrations (MPICs). The conversion requires knowledge of the molecular mass of the target gas.

DEFINITIONS

Absolute Background	An absolute backgrounds are either zero-path or synthetic backgrounds and will contain little or no absorption features.
CLS	Classical Least Squares, regression fit of measured absorbance to calibrated reference absorbance spectra.
${}^m\hat{C}_{mix}$	Arbitrated mass path-integrated concentration of alkane mixture, usually with units of ppb· meter or ppm·meter. usually with units of mg/m ² or g/m ² .
${}^v\hat{C}_x^A$	Volume path-integrated concentration of alkane component, x, analyzed in regions A ($A = LAL, HAL$ or <i>arbitrated</i>), usually with units of ppm·meter or ppb·meter.
HAL	High Alkane Level region of analysis, xxx to yyy cm ⁻¹ . This region contains weaker bands of n-butane and n-octane and is the region of choice when the alkane concentrations are high enough to distort the strong bands.
LAL	Low Alkane Level region of analysis, 2004.2 to 3001.2 cm ⁻¹ . This region contains the strong bands n-butane and n-octane bands, and is the region of choice for low concentration levels.
\overline{M}_{mix}	Mean molecular mass of the alkane mixture in units of g/mole
Relative Background	Background that was measured over the same path as the sample, single beams. These background spectra will produce absorbance spectra in which the atmospheric absorption bands will be wholly or nearly cancelled. In some cases these backgrounds may contain absorption features of the target species that may require correction.

INTRODUCTION: The shapes of the 3.3 μm absorption bands of the individual components of alkane mixtures, butane (C-4) to decane (C-10) are similar to each other. Figure 1 shows the comparison of the absorption bands of the straight-chain alkanes C-4 to C-8 (n-butane to n-octane). Starting with C-4, the similarity is greatest between the components with consecutive carbon numbers (e.g. butane and pentane) and the similarities decrease for components with greater difference in carbon numbers (e.g. C-4 and C-8, butane and octane). The similarity in band shapes makes it impossible to include all of the components of the mixture in the CLS analysis. The CLS multi-component regression analysis requires that the absorption bands of the co-analyzed species do not correlate, i.e. the band shapes of the components are not too similar. When the bands of two or more co-analyzed species correlate, the respective concentration determinations become unreliable.

For the past twenty years, the analysis of alkane mixtures has been performed using a surrogate to represent the total volume concentration of the entire mixture. The surrogate species was often n-octane, but in some cases another alkane was chosen because its band had a better fit to the shape of the mixture band. However this method results in a volume concentration and to convert to mass concentration, one had to estimate (or guess) the mean carbon number of the mixture.

The present method provides a direct measurement-based determination of the mean carbon number that is required in order to convert the VPIC of the mixture to MPIC values. We assume that the vapor emitted from the alkane mixture is mainly composed of C-4, C-5, C-6, C-7, C-8. The alkanes with carbon numbers less than 4 (methane, ethane and propane) are not expected to be components of the mixture because these species are gases at standard atmospheric conditions and if present upon manufacture, would have outgassed from the liquid fuel. Alkanes with higher carbon numbers than C-8 (nonane, decane, etc) have low vapor pressures and therefore would not be present in the vapor at significant levels.

The fuel-alkane analysis method involves analyzing two of the straight-chain alkanes members of C-4 to C-8 that have the least correlated absorption bands, n-butane and n-octane (C-4 and C-8). The correlation between these two bands, at 0.5 cm^{-1} resolution, is low enough to ensure a statistically valid regression fit (see Figure 2).

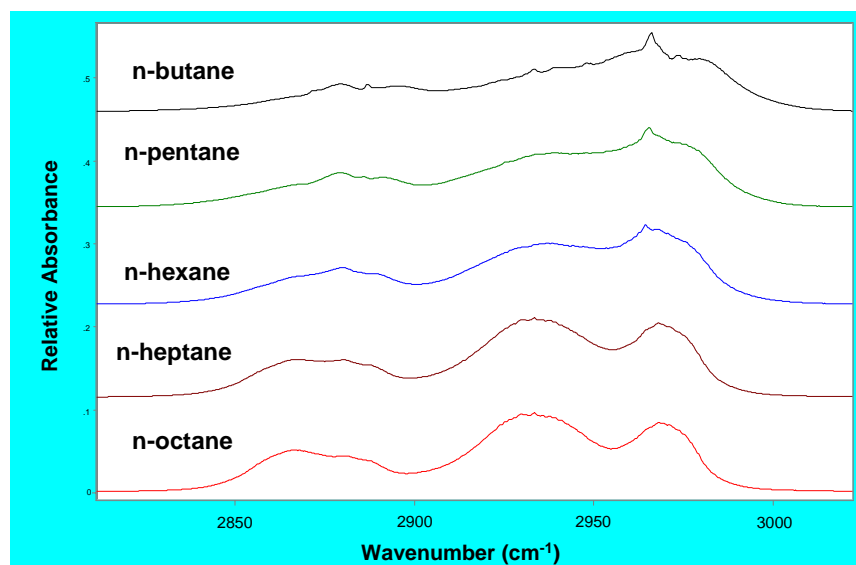


Figure 1. Comparison of the absorption bands of straight-chain alkanes, C-4 (n-butane) to C-8 (n-octane), measured with 0.5 cm^{-1} resolution.

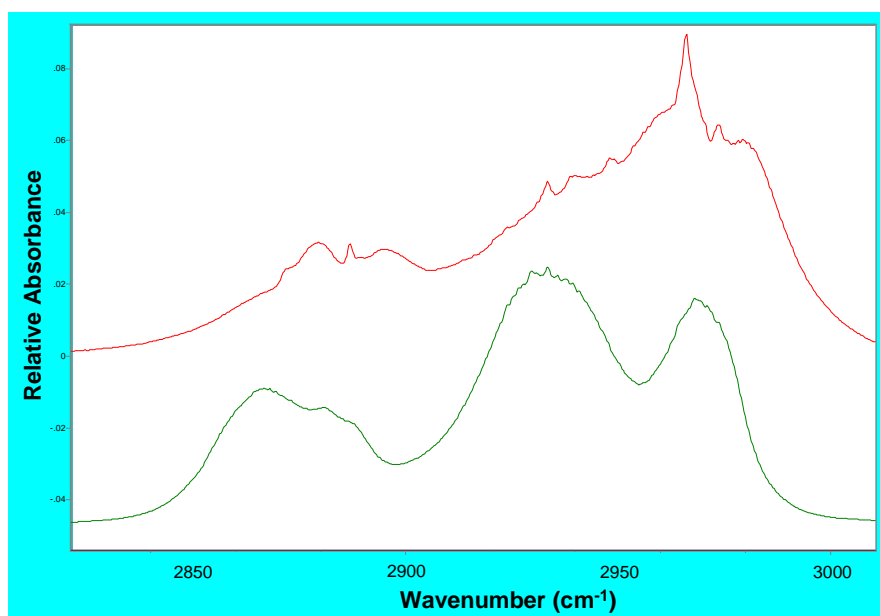


Figure 2. Comparison of the absorption bands of n-butane (red trace) and n-octane (green trace), measured with 0.5 cm^{-1} resolution.

1.0 PROCEDURE

1.1 Set Up Region(s) of Analysis. The OP-FTIR field measurements should be performed along with the QA/QC procedures described in the EPA ORS Facility Manual (ECPB 2004). The

primary region of analysis is 2004.2 to 3001.2 cm^{-1} . This region fully encumbers the main bands of the alkane mixture. If the path-average concentrations are expected to be high enough to distort the band-shapes, a second analysis, high alkane level (HAL) could be performed in the region from 2694.0 to 2915.7 cm^{-1} . Weaker bands of n-butane and n-octane lie in this region and they exhibit little correlation. Depending on the requirements of the field measurement, the HAL analysis could either be performed at the time of the measurements (in real-time) or in a post-measurement analysis.

1.2 Set Up the Chemical Species for Analysis. The Two analytes are n-butane and n-Octane. The atmosphere interferences are methane and water vapor. If other species might be present that have absorption bands in the regions of analysis (e.g. methanol, formaldehyde, etc), they should be included in the analysis as interferences, providing that their absorption bands do not correlate with either the n-butane or the n-octane bands.

1.3 Arbitration Rules for Combined LAL and HAL Analysis. This step only applies if both LAL and HAL analyses on n-butane and n-octane have been performed. The volume PIC for the alkane mixture, ${}^v C_{mix}^A$, is the sum of the CLS determinations for n-butane and n-octane in region A, and the standard error of the ${}^v C_{mix}^A$ determination is the square root of the sum of the squares of the respective standard error for the n-butane and n-octane determinations. Using labels to depict the LAL and HAL analyses, we have four metrics,

$${}^v C_{mix}^{LAL} = {}^v C_{bu\ tan\ e}^{LAL} + {}^v C_{oc\ tan\ e}^{LAL},$$

$$\sigma_{mix}^{LAL} = \sqrt{(\sigma_{bu\ tan\ e}^{LAL})^2 + (\sigma_{oc\ tan\ e}^{LAL})^2},$$

$${}^v C_{mix}^{HAL} = {}^v C_{bu\ tan\ e}^{HAL} + {}^v C_{oc\ tan\ e}^{HAL},$$

and

$$\sigma_{mix}^{HAL} = \sqrt{(\sigma_{bu\ tan\ e}^{HAL})^2 + (\sigma_{oc\ tan\ e}^{HAL})^2}.$$

The arbitration between using the LAL or the HAL determinations is made for each measurement in the set, according to the following logic conditions,

1. **IF** ${}^v \hat{C}_{mix}^{LAL} > 3 \cdot \sigma_{mix}^{LAL}$ **AND** ${}^v \hat{C}_{mix}^{HAL} > 3 \cdot \sigma_{mix}^{HAL}$
AND ${}^v \hat{C}_{mixture}^{HAL} > {}^v \hat{C}_{mixture}^{LAL}$
THEN ${}^v \hat{C}_{mixture}^{Arbitrated} = {}^v \hat{C}_{mixture}^{HAL}$
2. **IF** ${}^v \hat{C}_{mix}^{LAL} > 3 \cdot \sigma_{mix}^{LAL}$ **AND** ${}^v \hat{C}_{mix}^{HAL} > 3 \cdot \sigma_{mix}^{HAL}$

AND ${}^V\hat{C}_{mix}^{HAL} < {}^V\hat{C}_{mix}^{LAL}$

THEN ${}^V\hat{C}_{mix}^{Arbitrated} = {}^V\hat{C}_{mix}^{LAL}$

3. IF ${}^V\hat{C}_{mix}^{LAL} < 3 \cdot \sigma_{mix}^{LAL}$ **AND** ${}^V\hat{C}_{mix}^{HAL} > 3 \cdot \sigma_{mix}^{HAL}$

THEN ${}^V\hat{C}_{mix}^{Arbitrated} = {}^V\hat{C}_{mix}^{HAL}$

4. IF ${}^V\hat{C}_{mix}^{LAL} > 3 \cdot \sigma_{mix}^{LAL}$ **AND** ${}^V\hat{C}_{mix}^{HAL} < 3 \cdot \sigma_{mix}^{HAL}$

THEN ${}^V\hat{C}_{mix}^{Arbitrated} = {}^V\hat{C}_{mix}^{LAL}$

5. IF ${}^V\hat{C}_{mix}^{LAL} < 2 \cdot \sigma_{mix}^{LAL}$ **AND** ${}^V\hat{C}_{mix}^{HAL} < 2 \cdot \sigma_{mix}^{HAL}$

THEN ${}^V\hat{C}_{mix}^{Arbitrated}$ is below the Detection Limit

Criteria 1 and 2 address the issue of whether the strong band in LAL is saturated due to very high levels of alkanes. If saturation occurs, then the band intensity will grow at a rate that is less than linear resulting in a concentration determination that is less than the value that would occur if linearity prevailed. In this case one would expect that the analysis in the HAL region (where the bands are much weaker and more likely to maintain linearity) would yield a higher determination than in the saturated LAL region. This leads to the criterion, if both analysis results are above detection limits one chooses higher value. However, as stated below in the section on QA/QC, the analyst must validate the results in the HAL region when the concentration determinations are not much above detection limits.

1.4 Determination of the Mean Molecular Mass, \overline{M}_{mix} ,

The mean molecular mass of the alkane mixture, \overline{M}_{mix} , is given as

$$\overline{M}_{mix} = \frac{M_{butane} \cdot {}^v\hat{C}_{butane}^{Arbitrated} + M_{octane} \cdot {}^v\hat{C}_{octane}^{Arbitrated}}{{}^v\hat{C}_{mix}^{Arbitrated}}, \quad (1)$$

where $M_{butane} = 58.12$ g/mole (molecular mass of butane),

$M_{octane} = 114.23$ g/mole (molecular mass of octane),

${}^v\hat{C}_{butane}^{Arbitrated}$ and ${}^v\hat{C}_{octane}^{Arbitrated}$ are the butane and octane determinations from the analysis of the arbitration-chosen region.

1.5 Determination of the Mass Path-Integrated Concentration, ${}^m\hat{C}_{mix}$,

The mass path-integrated concentration of the alkane mixture, ${}^m\hat{C}_{mix}$, is given as

$${}^m\hat{C}_{mix} = \frac{L(T, P) \cdot \overline{M}_{mix}}{A} \cdot {}^v\hat{C}_{mix}^{Arbitrated}$$

Where $L(T)$ is Loschmidt's Number at temperature, T and pressure P ,

$$L(T) = 2.4793 \times 10^{25} \cdot \frac{296K}{T} \cdot \frac{P}{1 \cdot atm} \text{ molecules/m}^3,$$

and A is Avogadro's number, 6.0220×10^{23} molecules/mole. The numerical solution is

$${}^m\hat{C}_{mix} [g / m^3] = 4.1171 \times 10^{-5} \cdot \overline{M}_{mix} \left(\frac{296K}{T} \right) \left(\frac{P}{1 \cdot atm} \right) {}^v\hat{C}_{mix}^{Arbitrated} [ppm] \quad (2)$$

The procedure for converting the volume PICs of alkane vapor mixtures from petroleum-base fuels to mass PIC is summarized by Equations 1 and 2.

2.0 QA/QC CHECKS ON THE ANALYSIS

The QA/QC checks on the analysis must be carried out as a post-measurement procedure. If in performing the QA/QC checks, one finds quality problems that degrade the precision and accuracy analytical results to levels below those permitted by the Data Quality Objectives (DQOs) of the field project, the analysis should be repeated with corrections.

2.1 Check the Background Spectra

The QA/QC procedure on Relative Backgrounds is different than the procedure for Absolute Backgrounds. The Relative Backgrounds may contain the absorption bands due to the alkane, which would produce a negative bias on the alkane determinations. Many of the OP-FTIR systems produce single-beam spectra that have inherent hydrocarbon bands present, due to adsorption of oils on the optical surfaces. These “oil” bands are cancelled out in zero-path backgrounds, but may be present in the field absorbance spectra that were created using synthetic backgrounds. Therefore the QA/QC check on the zero-path Background should follow the same procedure as for Relative Backgrounds.

2.1.1 Relative and Zero-Path Backgrounds

1. Create Synthetic Backgrounds

For each Relative Background create an associated synthetic background, taking care not to place any points in the region between 2804 and 3002 cm^{-1} .

2. Create Absorbance Spectra

For each Relative Background create a absorbance spectrum using the relative background as the sample single beam and the synthetic background as the background.

3. Analyze Absorbance Spectra

Analyze each of the absorbance spectra for the alkanes using the same method as used for the field measurement. Record the results as part of the QA/QC report.

4. Correct Path-Integrated Concentrations (If Necessary)

If the path-integrated concentrations for n-butane and/or n-octane determined in Step 3 are above detection limits, determine whether the values are significant compared to the values determined on the field data. If they are, correct the field measurements by adding the background values that are above detection limits to the corresponding field values for n-butane and n-octane in the respective LAL and HAL regions. If corrections were made, then repeat the arbitration and mass integrated concentration determination procedures in Steps 1.3 to 1.5, above.

2.1.2 Synthetic Backgrounds

1. Prepare an Absorbance Spectrum from Alkane-Free Single Beam

Create an absorbance spectrum using any available single-beam spectrum that was measured (in the time period of the project) in an environment in which no hydrocarbons were present in the atmosphere and using the synthetic background as the background. Unless there is expectation that the adsorbed oils on the OP-FTIR optics will change over the course of the project, only one absorbance spectrum will be necessary for this check for the entire project.

2. Analyze Absorbance Spectra

Follow Step 3 in Section 2.1.1

3. Correct Path-Integrated Concentrations (If Necessary)

Follow Step 4 in Section 2.1.1

A single-beam spectrum from the project’s quality assurance procedures could be used.

2.2 Check for Interfering Absorption Features

Check the LAL spectral region (and HAL region if used) for the presence of overlapping absorption bands by outlier species. Look for features that deviate from the band shapes of the C-4 to C-8 species shown in Figure 1. Search the Finger Print Region (723 to 1400 cm^{-1}) for absorption bands or lines due to the presence of unexpected species. If any are found determine if there are corresponding C-H stretch bands.

Add all the spectral references of any species, which have been found to have overlapping bands in the LAL region (or HAL region if used), to the CLS analysis as interferents. This procedure needs to be performed only on measurement sets in which the outlier features are present and cause the data quality to not meet the project DQO.

2.3 Check for Saturation in the LAL Region

Determine if any of the measured alkane absorption bands in the LAL region exhibit saturation. Generally, these bands become saturated at path-integrated concentration levels greater than $2000\text{ ppm}\cdot\text{m}$. Saturation can be recognized by view the peak band features and noting if they have a flattened appearance. This effect can be seen in Figure 3, which shows a saturated alkane mixture band measured at a refinery compared to a measured band that is still in the linear regime. The absorbance scales are different for the two traces. The scale for the green trace is greatly expanded compared to the red trace. If saturation is detected, then the analysis must be performed in the HAL region and the results must follow the arbitration procedure listed in Section 1.3.

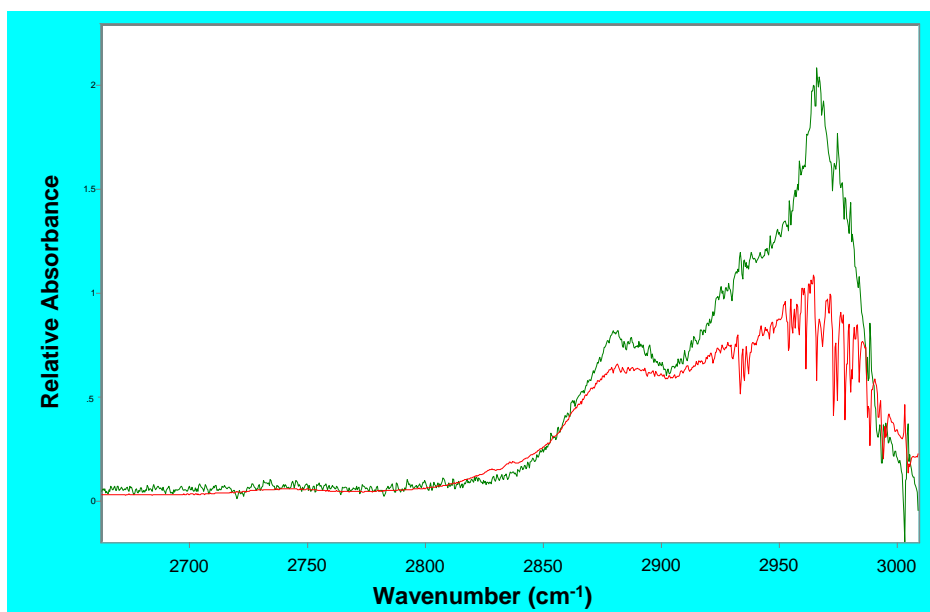


Figure 3. Comparison of a saturated alkane-mixture band (red trace) to one that is not saturated (green trace). The two traces are on plotted on the same ordinate scale. Note the difference in noise.

2.4 If Using HAL Region Check Arbitrated HAL Values Close to Detection Limits

Check all arbitrated values close to detection limits are valid. These values should smoothly transition to the lower values that arbitrate towards LAL. If these results seem to not connect to the HAL arbitrated values smoothly, then one may consider raising the detection-limit criterion for the HAL values $4\cdot\sigma$ or greater.

3.0 REFERENCE

ECPB 2004 ECPB (Emission Characterization Prevention Branch) Optical Remote Sensing Facility Manual, Prepared for the US EPA NRMRL Revision 1 April 2004